

# High-Capacity, Low-Voltage Titanate Anodes for Sodium-Ion Batteries

Project ID # BAT428

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2020 DOE Vehicle Technologies Office Annual Merit Review

# Overview

## Timeline

- Project start date 10/1/2018
- Project end date 9/30/2021
- Percent complete 60 %

## Budget

- Total project funding
  - DOE share 100 %
  - Contractor share N/A
- Funding for FY2019 \$ 300 k
- Funding for FY2020 \$ 300 k

## Barriers and Technical Targets

- Barriers addressed
  - Supply issues with Li and Co
  - Cost
  - Safety and rate capability

## Partners

- LBNL, Army Research Lab
- Project lead: Marca M. Doeff

# Relevance

- ❑ Na-ion batteries are a possible drop-in replacement for Li-ion batteries
  - Similarity in concept means we can leverage engineering knowledge (closest "beyond lithium ion" system to commercialization).
  - Co-free cathodes are available for Na-ion batteries (the ethics of Co mining are an issue for Li-ion batteries, as well as its cost).
  - Na-ion anodes do not require Cu current collectors, can use Al. This lowers cost and alleviate concerns about Cu, another strategic metal.
  - Na-ion electrolytic solutions are generally 10-15% more conductive than their Li-ion analogs. Can use less electrolyte salt (a cost savings), and/or design cells with thicker electrodes without compromising the energy/power ratio, another cost-savings.
  - State-of-the-art Na-ion batteries exceed energy densities of Li-ion batteries with  $\text{LiFePO}_4$  cathodes.
- ❑ Need better anodes for Na-ion batteries
  - Safety concerns with the hard carbon anodes currently used.
  - Energy density is dependent on anode material (we have good cathodes).
  - Goal of this project is to investigate the possibility of titanate anodes, another goal is to study electrolytes that can enable these electrodes.

# Milestones-FY2019

Milestone	Type	Date/Status
Hydrothermal synthesis of sodium nonatitanate	Milestone	Q1/Completed
Ion exchange sodium nonatitanate with Mg	Milestone	Q2/Completed
Complete synchrotron XRD and XAS	Milestone	Q3/Completed
Go/no go decision on Mg exchange	Go/no go	Q4/No go, because Mg exchange worsen properties.

Any proposed future work is subject to change based on funding levels

# Milestones-FY2020

Milestone	Type	Date/Status
SEI studies and electrolytes (XPS, XAS, ATR-FTIR)	Milestone	Q1/Underway
Synthesize lepidocrocite titanates	Milestone	Q2/Completed
Select best electrolyte solution	Milestone	Q3/Planned
Go/no go decision on sodium nonatitanate	Go/no go	Q4/Planned, stop if material doesn't achieve goals.

Any proposed future work is subject to change based on funding levels

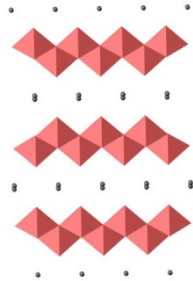
# Milestones-FY2021

Milestone	Type	Date/Status
Characterize lepidocrocite titanates	Milestone	Q1/Planned
Optimize electrodes (carbon content, binder, etc.)	Milestone	Q2/Planned
Assemble, test and study full cells	Milestone	Q3/Planned
Go/no go decision on lepidocrocite titanates	Go/no go	Q4/Planned, stop if material doesn't achieve goals.

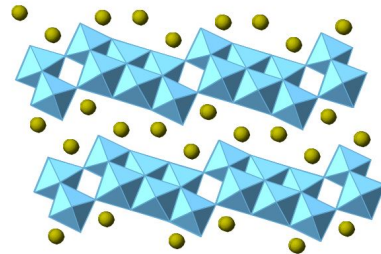
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# Approach

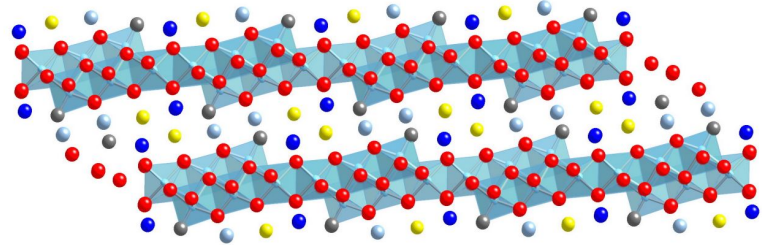
- Candidate titanate anode materials are synthesized and studied.
- Several techniques are used to understand their sodium insertion mechanisms and their interfacial properties. These include *in situ* synchrotron XRD, XAS, XPS and other spectroscopic techniques.
- Some work will be directed towards development of electrolytes and additives (with Dr. Kang Xu of Army Research Lab and understanding their effects on interfacial chemistry.



Lepidocrocite-type  
Step-size=1



$\text{Na}_2\text{Ti}_3\text{O}_7$   
Step-size=3



Sodium nonatitanate ( $\text{NaTi}_3\text{O}_6\text{OH}$ )  
Step-size=6

# Background

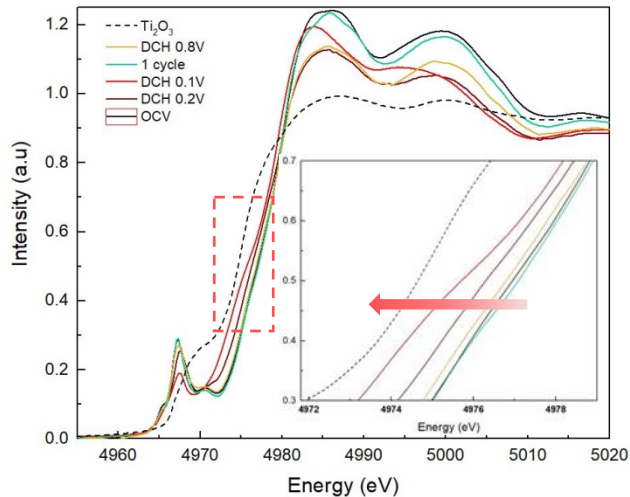
- There are several corrugated layered Na-Ti-O titanates that can reversibly insert Na ions.
  - We have chosen 3 to study initially (see Approach) based on their structural similarities but quite different electrochemical behavior.
    - **Lepidocrocite-structured titanates.** Step size=1. Variable compositions,  $A_xTi_{2-y}M_yO_4$ ; A=large cation, M=vacancy, Li, Mg, Co, Ni, Fe, Mn, Cu, Zn, etc. Sloping featureless voltage profiles, similar to supercapacitor with  $V_{av} \approx 0.5V$  vs. Na/Na<sup>+</sup>. See M. Shirpour, *et al.* Chem. Mater. 2014, 26, 2502.
    - **Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>.** Step size=3. Flat voltage profile at  $\sim 0.3V$  vs. Na/Na<sup>+</sup>. Two-phase behavior. See P. Senguttuvan *et al.* Chem. Mater. 2011, 23, 4109.
    - **"Sodium nonatitanate" NaTi<sub>3</sub>O<sub>6</sub>(OH).** Step size=6. Sloping featureless voltage profile, similar to supercapacitor with  $V_{av} \approx 0.3V$  vs. Na/Na<sup>+</sup>. See M. Shirpour, *et al.* Energy & Environ. Sci. 2013, 6, 2538.
- Questions we would like to answer
  - Is the electrochemical mechanism of lepidocrocite structured titanates and sodium nonatitanate different from Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (supercapacitor vs. insertion)?
  - If so, why?
  - Can we exploit supercapacitor behavior to improve energy density?
  - How do the step size differences relate to the electrochemistry? Can we design other materials based on the information we obtained?



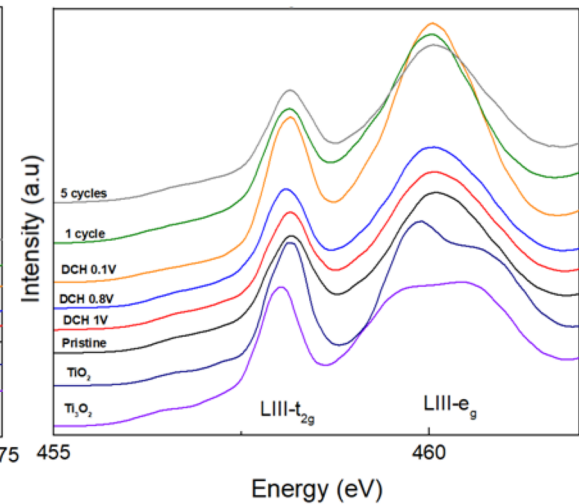
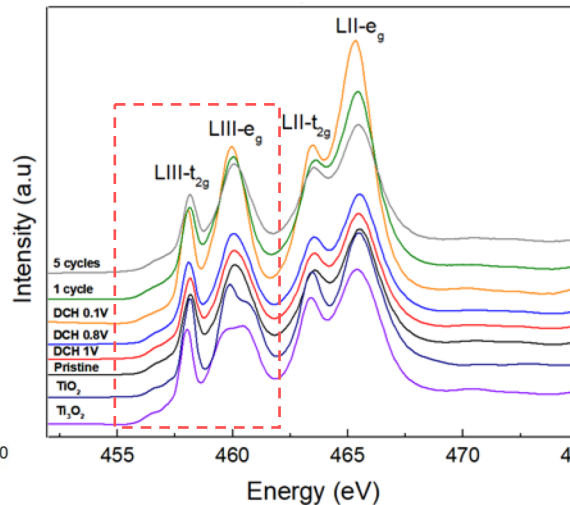
# Technical Accomplishments

## Understand the reaction mechanism of sodium nonatitanate electrode

Ti K-edge hard XAS spectra  
- bulk Ti oxidation state



Ti L-edge soft XAS spectra - surface Ti oxidation state

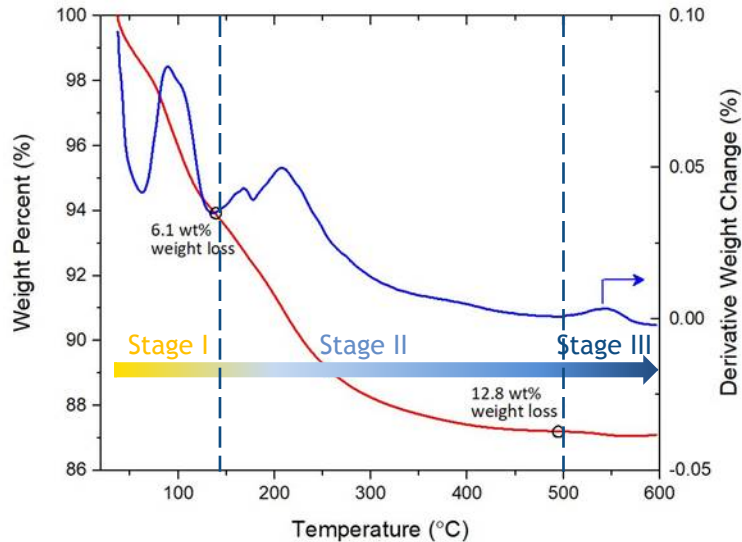


- Hard/soft XAS analyses reveal ubiquitous Ti redox reaction from surface to bulk, excluding pseudocapacitance as the main reaction mechanism.
- At the end of the first cycle, Ti oxidation state is slightly lower than the pristine state.

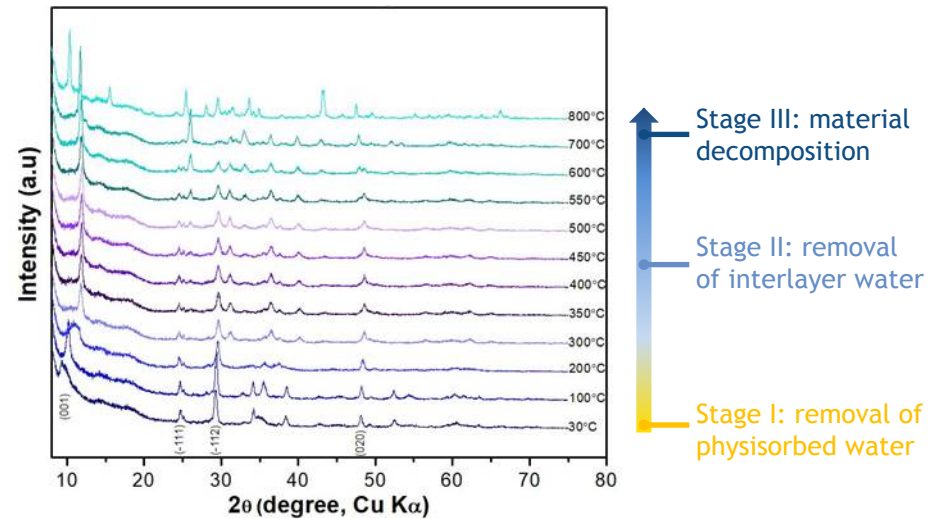
# Technical Accomplishments

## Optimized synthesis of sodium nonatitanate – critical dehydration step

Thermogravimetric Analysis  
of sodium nonatitanate



Temperature-dependent XRD  
data of sodium nonatitanate



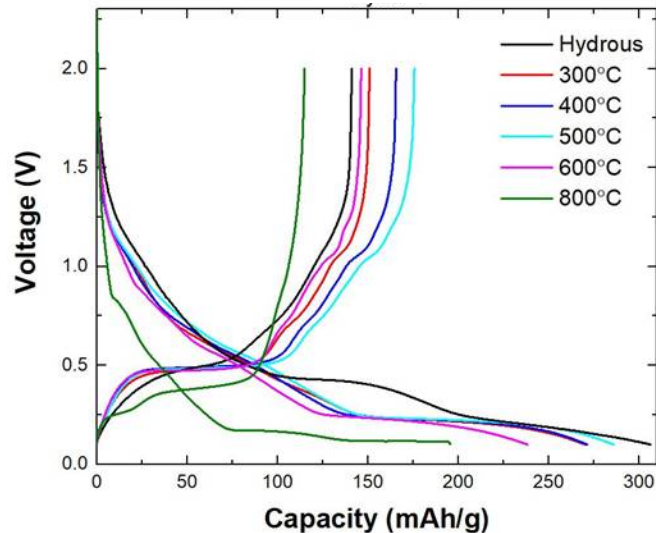
- Combined TGA and Temperature-dependent XRD analysis reveals gradual and complex structural change and weight loss.

# Technical Accomplishments

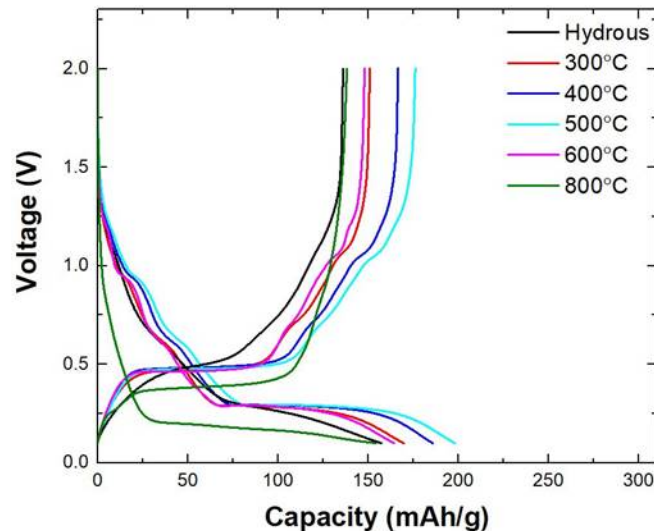
## Improved electrochemical performance – optimized dehydration temperature

Charge-discharge voltage profiles

Cycle 1



Cycle 2

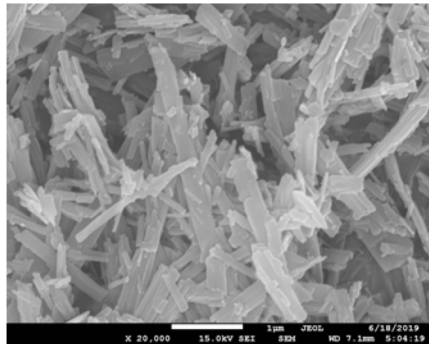


- Electrochemical properties evaluated in half-cells with sodium nonatitanate electrodes dehydrated at various temperatures.
- Dehydration at 500 °C gives the highest capacity.

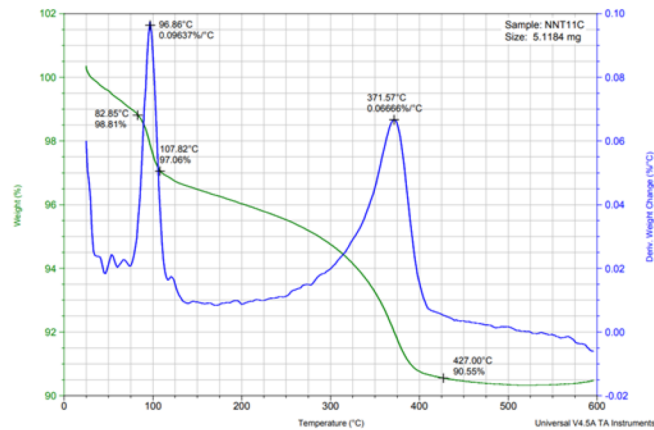
# Technical Accomplishments

## Improved electrochemical performance – carbon coating & binder optimization

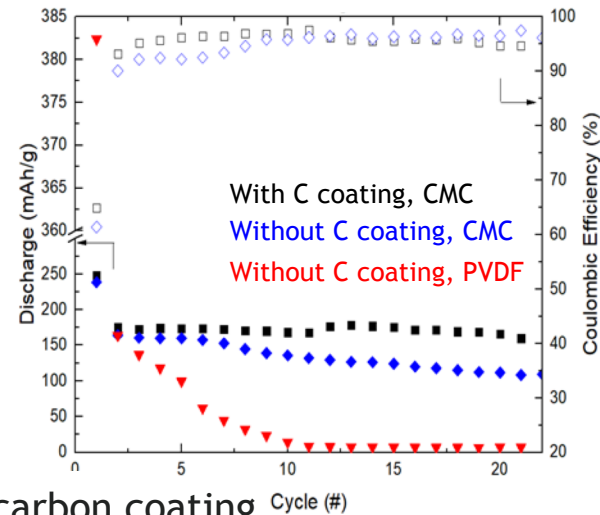
SEM image of carbon-coated sodium nonatitanate



Thermogravimetric Analysis of carbon-coated sodium nonatitanate



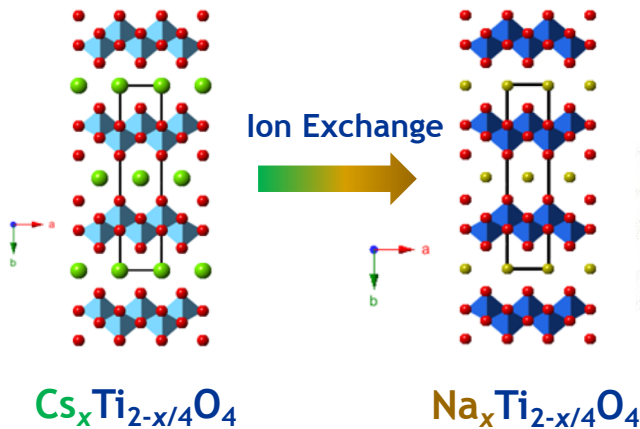
Discharge capacity retention and Coulombic efficiency



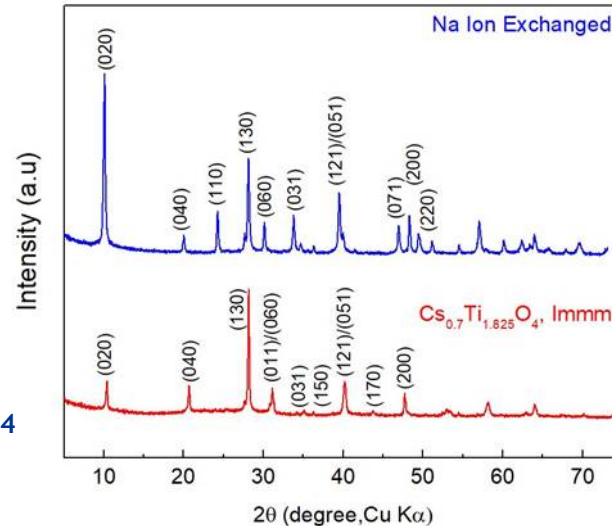
- The nano-rod shape of sodium nonatitanate is preserved after carbon coating.
- TGA result reveals the mass of carbon coating layer is ~6.51wt.%.
- The cycling stability of sodium nonatitanate electrode is greatly improved by the carbon coating layer and the use of CMC binder, exhibiting a discharge capacity of 160 mAh/g and 90% retention after 20 cycles.

# Technical Accomplishments

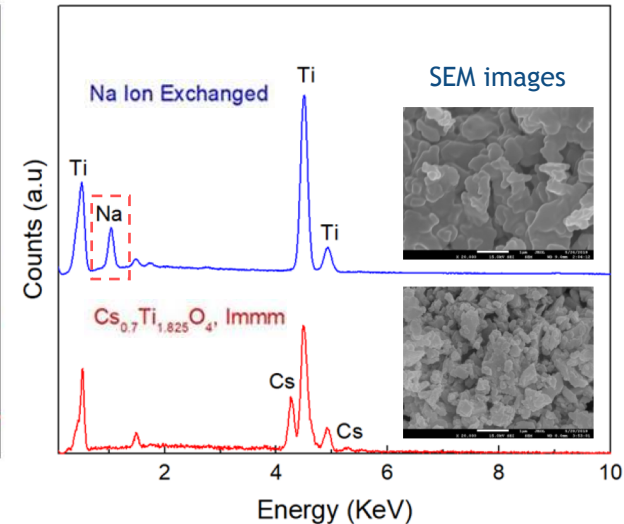
## Synthesis of lepidocrocite-structured titanates



Laboratory X-ray diffraction



Energy Dispersive X-Ray Spectroscopy

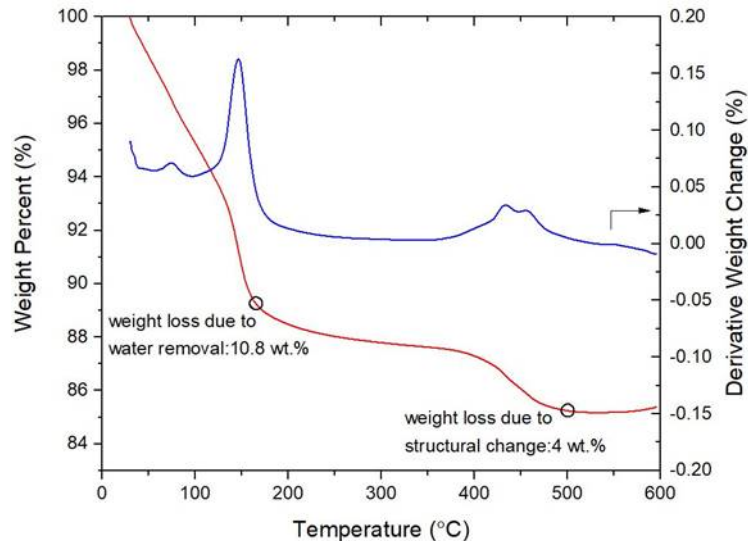


- Lepidocrocite-structured  $\text{Na}_{0.7}\text{Ti}_{1.825}\text{O}_4$  was synthesized via a two-step process: solid-state synthesis of  $\text{Cs}_{0.7}\text{Ti}_{1.825}\text{O}_4$  followed by Cs/Na ion-exchange, the successful Cs/Na ion-exchange is confirmed by EDS result.

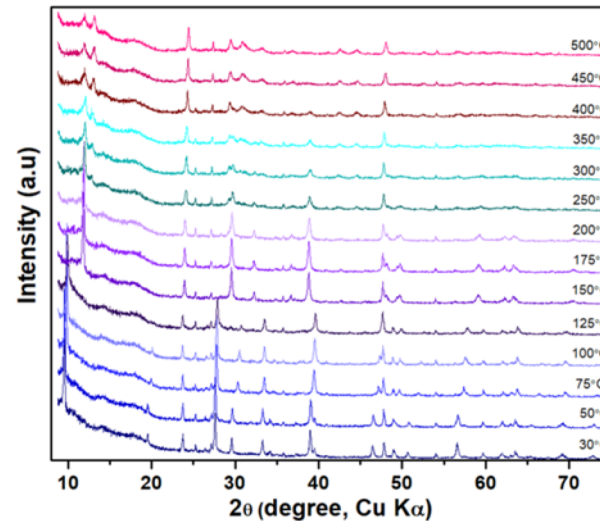
# Technical Accomplishments

## Structural stability of lepidocrocite-structured titanate

Thermogravimetric Analysis  
of lepidocrocite-type titanate



Temperature-dependent XRD  
data of lepidocrocite-type titanate

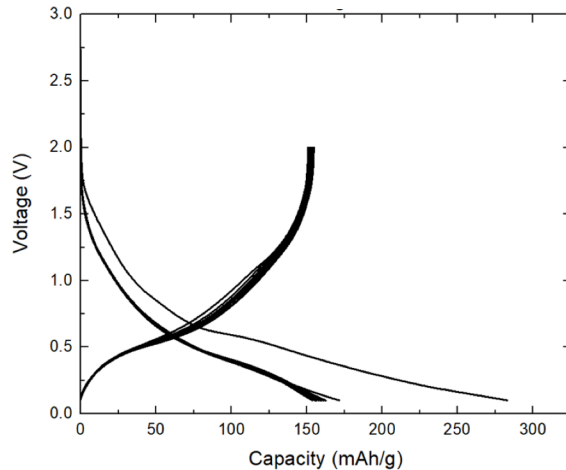


- Water removal from the structure is observed from ~125°C, drastic structural change occurs above ~350°C, resulting in a new phase formation.

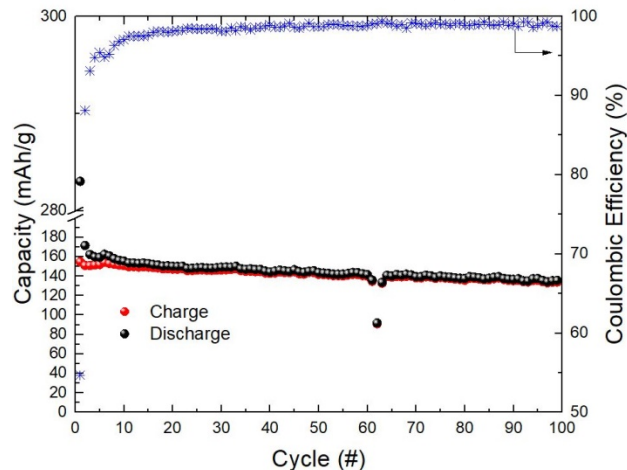
# Technical Accomplishments

## Electrochemical characterization of lepidocrocite-structured titanate

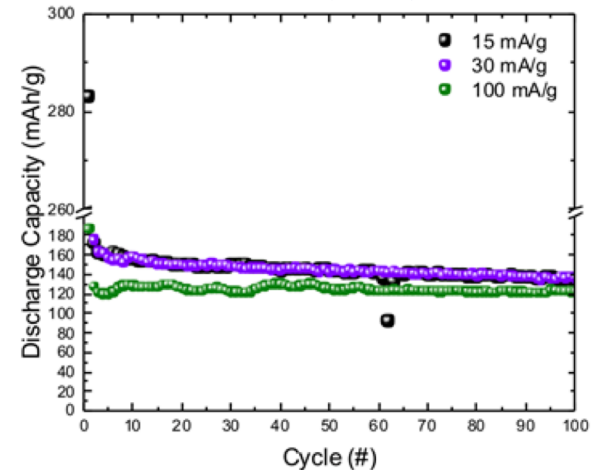
Charge-discharge voltage profiles



Capacity retention and coulombic efficiency



Discharge capacity retention at various cycling rates



- Lepidocrocite-type  $\text{Na}_{0.7}\text{Ti}_{1.825}\text{O}_4$  shows sloping and featureless voltage profiles with discharge capacities of 160-175 mAh/g from the second cycle on.
- Lepidocrocite-structured titanate electrodes exhibit decent rate capability when cycled in half-cells at different current rates.

# Response to Previous Year Reviewers' Comment



*Not Available*



# Collaborations

Collaborator	Role
Kang Xu, Army Research Lab	Electrolyte studies
Daniel Rettenwander and Maria Gombotz, TU Graz	NMR studies
Dennis Nordlund, Apurva Mehta, SSRL	Synchrotron XAS and XRD studies
Isaac Markus, IBM	DFT calculations

# Remaining challenges and barriers

- ❑ Great improvements have been made on improving the capacity and cycling stability of sodium nonatitanate electrodes at electrode level, how can it be further improved at the cell level (e.g., optimize their compatibility with electrolyte solution)?
- ❑ Further optimize the lepidocrocite-structured titanate electrode, the focus will be not only on mitigating its intrinsic electronic conductivity, but also on alleviating the parasitic reactions related to each of the electrode components.
- ❑ Identify the sodium storage mechanism of lepidocrocite structured titanate, and compare with those of sodium nonatitanate and  $\text{Na}_2\text{Ti}_3\text{O}_7$ , so as to understand if their different step sizes significantly affect the reaction mechanisms.
- ❑ The interfacial chemistry of these titanate electrodes needs to be understood.
- ❑ The electrochemical properties of titanate electrodes at the full-cell level may be evaluated.

# Proposed Future Work



- ❑ Select better electrolyte solution (salt, solvent, additives) for sodium nonatitanate electrode, and understand the interfacial chemistry by employing surface-sensitive synchrotron techniques.
- ❑ Finish the synthesis of a series of lepidocrocite-structured titanates, and investigate the effect of composition variables on their electrochemical properties.
- ❑ Further optimize the lepidocrocite-structured titanate electrodes by addressing the electronic conductivity limitation and degradation issue, assemble full cells with compatible cathode material, and evaluate their performance (e.g., capacity, energy density, cycling stability, power density) as well as study interfacial chemistry which can be drastically different from their half-cell counterparts.

"Any proposed future work is subject to changes based on funding levels."

# Summary



- ❑ With combined hard/soft X-ray adsorption spectroscopy experiments, the main sodium storage mechanism of sodium nonatitanate is determined to be bulk and surface Ti reduction.
- ❑ Sodium nonatitanate electrode has been optimized in three regards: 1) selected the best hydration temperature, 2) created a carbon coating layer at the surface, and 3) choose a better CMC binder.
- ❑ Lepidocrocite-structured titanate electrode materials have been successfully synthesized, its structural stability was evaluated to be stable up to  $\sim 125^{\circ}\text{C}$ .
- Electrochemical characterization in half-cell configuration shows that lepidocrocite-structured titanate electrodes deliver a discharge capacities of 160-175 mAh/g from the second cycle on with good rate capability.